

DECLARATION

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do hereby solemnly and sincerely declare:

- 1) THAT I am well acquainted with the Japanese language  
and English language, and
- 2) THAT the attached is a full, true, accurate and  
faithful translation into the English language made  
by me of Japanese Patent Application No. 2004-018472.

The undersigned declares further that all  
statements made herein of his own knowledge are true and  
that all statements made on information and belief are  
believed to be true; and further that these statements  
were made with the knowledge that willful false statements  
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or both, under section 1001, of Title 18 of the United  
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jeopardize the validity of the application or any patent  
issuing thereon.

Signed this 6<sup>th</sup> day of October, 2009.

  
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[Kind of Document]     Claims

[Claim 1]

          A process for producing a laser engravable flexographic printing original plate, characterized by comprising the steps of: forming a photosensitive resin composition layer on a cylindrical support or a sheeted support; applying light to the formed photosensitive resin layer to form a cured laser engravable photosensitive resin layer; and then adjusting a thickness of the cured photosensitive resin layer and shaping a surface of the cured photosensitive resin layer, wherein the light applied to the photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

[Claim 2]

          The process for producing a laser engravable flexographic printing original plate according to claim 1, characterized by further comprising a step of applying light to the cured photosensitive resin layer again after the step of adjusting a thickness of the cured photosensitive resin layer and shaping a surface of the cured photosensitive resin layer, wherein the light again applied to the cured photosensitive resin

layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the cured photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark  
5 "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

[Claim 3]

The process for producing a laser engravable  
10 flexographic printing original plate according to claim 1 or 2, characterized in that atmosphere in which the light is applied to the photosensitive resin layer or the cured photosensitive resin layer is air.

[Claim 4]

15 The process for producing a laser engravable flexographic printing original plate according to claim 1, 2 or 3, characterized in that the photosensitive resin layer is liquid at 20°C.

[Claim 5]

20 The process for producing a laser engravable flexographic printing original plate according to any of claims from 1 to 4, characterized in that the photosensitive resin layer and the cured photosensitive layer comprise an inorganic porous material (c).

25 [Claim 6]

The process for producing a laser engravable flexographic printing original plate according to any of claims from 1 to 5, characterized in that the cured

laser engravable photosensitive resin layer is a seamless layer.

[Claim 7]

The process for producing a laser engravable flexographic printing original plate according to any of claims from 1 to 6, characterized in that the photosensitive resin composition comprises a photopolymerization initiator which contains a hydrogen extraction photopolymerization initiator and a collapse photopolymerization initiator.

[Claim 8]

The process for producing a laser engravable flexographic printing original plate according to claim 7, characterized in that the hydrogen extraction photopolymerization initiator consists of at least one type of compounds selected from benzophenones, xanthenes and anthraquinones, and the collapse photopolymerization initiator consists of at least one type of compounds selected from benzoinalkyl ethers, 2,2-dialkoxy-2-phenyl acetophenones, acyloxime esters, azo compounds, organic sulfur compounds and diketones.

[Claim 9]

The process for producing a laser engravable flexographic printing original plate according to claim 5, characterized in that the inorganic porous material (c) has an average pore diameter from 1 nm or more to 1000 nm or less, a pore volume from 0.1 ml/g or more to 10 ml/g or less, a specific surface area from 10 m<sup>2</sup>/g or

more to 1500 m<sup>2</sup>/g or less and an oil absorption from 10 ml/100 g or more to 2000 ml/100g or less.

[Claim 10]

The process for producing a laser engravable  
5 flexographic printing original plate according to claim  
5 or 9, characterized in that the inorganic porous  
material (c) has a number average particle diameter from  
0.1 µm or more to 100 µm or less, and at least 70% of  
the particles are spherical particles having a  
10 sphericity from 0.5 to 1.

[Claim 11]

The process for producing a cylindrical laser  
engravable flexographic printing original plate  
according to any of claims from 1 to 10, characterized  
15 in that the photosensitive resin composition comprises a  
resin (a) having a number average molecular weight of  
1000 or more and 200000 or less, an organic compound (b)  
having a number average molecular weight of less than  
1000 and having a polymerizable unsaturated group in its  
20 molecule, and an inorganic porous material (c).

[Claim 12]

The process for producing a cylindrical laser  
engravable flexographic printing original plate  
according to claim 11, characterized in that 20 wt% or  
25 more of the total amount of the organic compound (b) is  
the derivative of at least one type of alicyclic  
compounds or aromatic compounds.

[Kind of Document]      Description

[Title of the Invention]      PROCESS FOR PRODUCING LASER  
   ENGRAVABLE FLEXOGRAPHIC  
   PRINTING ORIGINAL PLATE

5    [Technical Field]

[0001]

                                 The present invention relates to a process for  
producing a laser engravable cylindrical or sheeted  
flexographic printing original plate, which is suitable  
10    for formation of a relief image for a flexographic  
printing plate by laser engraving, formation of a  
pattern for surface processing such as embossing,  
formation of a relief image for printing of a tile or  
the like, printing a pattern of a conductor, a  
15    semiconductor or an insulator in formation of an  
electronic circuit, formation of a pattern of a  
functional material such as antireflection film of an  
optical component, a color filter or a (near) infrared  
cut filters, and further, coating and formation of a  
20    pattern of an oriented film, a ground layer, a  
luminescent layer, an electron transport layer or a  
sealing material layer in production of a display  
element of a liquid crystal display, an organic  
electroluminescence display or the like.

25    [Background Art]

[0002]

Flexographic printing is used for packaging materials such as corrugated boards, paper containers, paper bags and flexible packaging films, building and decoration materials such as wallpapers and decorative plates, label printing and the like. It has an increased proportion among various kinds of printing processes. For fabrication of printing plates for these uses, photosensitive resins are normally used. A process has been used, in which a photo mask is placed on a liquid photosensitive resin or a solid photosensitive resin plate in the form of a sheet, light is applied through the mask to cause a crosslinking reaction, and non-crosslinked parts are then washed out with a developing solution. In recent years, so called a flexographic CTP technique of providing a thin light absorption layer called a black layer on the surface of a photosensitive resin, irradiating laser light to the layer to form a mask image directly on a photosensitive resin plate, then irradiating light through the mask to cause a crosslinking reaction, and then washing out non-crosslinked parts of areas to which no light is applied, has been developed. It has been increasingly employed in terms of the effect of improving efficiency of fabrication of a printing plate. However, this technique has a limited effect of improving the efficiency because of requiring a developing step. So a technique is desired in which a relief image is formed directly on a printing original plate using laser and no



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developing step is required.

[0003]

One process for solving the problem is a process in which a printing original plate is directly  
5 subjected to laser engraving. Fabrication of letterpress printing plates and stamps by this process has already been conducted. Various materials for use in this process are known.

For example, Patent Document 1 (JP-B-47-5121  
10 (U.S. Patent No. 3549733)) discloses the use of polyoxymethylene or polychloral. Also in Patent Document 2 (JP-A-10-512823 (Ger. Patent No. A19625749)), the use of a silicone polymer or a fluorosilicone polymer is described, but photosensitive resins are not  
15 used.

[0004]

A cylindrical printing original plate for laser engraving using cross-linked rubbers has been known. The preparing process of the cylindrical rubber  
20 plate essentially requires the steps of coating fluid rubber material on cylindrical support, heat-curing by vulcanization and grinding the surface. In addition to these troublesome steps it has a crucial problem of requiring a lot of time for the stabilization of cross-  
25 linking.

[0005]

Patent Document 3 (JP-A-2001-121833 (European Patent Laid-Open No. 1080883)) has a description of

using a silicone rubber and compounding carbon black into it as an absorber of laser beam, but photosensitive resins are not used.

In Patent Document 4 (JP-A-2002-3665)  
5 elastomer materials mainly composed of ethylene are used, but photosensitive resins are not used. The curing rate of these materials by heating is slow and so the accuracy of film formation is not good.

[0006]

10 On the other hand, Patent Document 5 (Japanese Patent No. 2846954 (U.S. Patent No. 5798202)) and Patent Document 6 (Japanese Patent No. 2846955 (U.S. Patent No. 5804353)) disclose use of a material prepared by mechanically, photochemically and thermochemically  
15 reinforcing a thermoplastic elastomer such as SBS, SIS or SEBS. When engraving a thermoplastic elastomer by using a laser with an oscillation wavelength in an infrared range, a highly precise engraving pattern can not be formed because the resin is made melted outside  
20 the part of the laser beam diameter by heating. For this reason, it is said essential to mechanically reinforce the thermoplastic elastomer layer by adding a filler to it. In this patent, the carbon black highly effective to mechanically reinforce it is mixed for the  
25 purpose of mechanically reinforcing the thermoplastic elastomer layer and improving the absorption of the laser light. However, the carbon black mixed sacrifices permeability of light when trying to photochemically

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reinforce it by using light. Therefore, in engraving these materials by laser the debris (including liquid sticky substance) hard to remove is produced in a large amount. This requires a lot of time to treat, also  
5 makes the relief rise at an edge by melting, makes the edge dragging and unclear and causes disadvantages of destroying the form of fine dots. Moreover, there is no description in this patent about the illuminance of light used in the photo-curing process and properties of  
10 the cured photosensitive resins obtained by applying light of a high illuminance source for photo-curing.  
[0007]

Especially when a large amount of liquid debris is produced that presumably is a degraded product  
15 of the resin in laser engraving, it contaminates the photo-system of a laser apparatus, also generates baked stains of the liquid resins attached to the surface of the photo components such as lens and mirror and causes serious troubles on the apparatus. In Patent Document 7  
20 (JP-A-2003-526697), there is a description about a laser engraving printing original plate using a liquid photosensitive resin composition, in which a liquid debris produced in a large amount in laser engraving is removed by using an inorganic porous material. However,  
25 there is no description about the properties of the cured photosensitive resin obtained by applying UV light of high illuminance for photo-curing.  
[0008]

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In general, the exposing apparatus used in forming a flexographic printing plate from photosensitive resins has a light source with an extremely narrow wave range such as a chemical lamp,  
5 having a central wavelength from 350 nm to 380 nm and a half bandwidth of the emission wavelength in the order of 10 nm to 20 nm. It seems that the essential requirement to form a fine pattern is achieved by using a light source with such a narrow wave range. Also in  
10 forming a fine pattern, it is general not to use a light source of extremely high illuminance in terms of formability of the pattern. Illuminance of light from these light sources is about 10 mW/cm<sup>2</sup> when measured using the UV meter (trade mark "UV-M02" manufactured by  
15 ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 0 mW/cm<sup>2</sup> when measured using the UV meter and UV-25 Filter.  
[0009]

Various materials for laser engraving have been hitherto proposed as described above, and methods  
20 for photo-curing photosensitive resin compositions are known. However, a laser engravable printing original plate is not known that makes use of the cured photosensitive resin which is obtained by applying UV light of high illuminance to the photosensitive resin  
25 composition to photo-cure. According to the illuminance of the light source used, properties and surface conditions of the photo-cured material formed are seriously different.

[Patent Document 1] JP-B-47-5121  
[Patent Document 2] JP-A-10-512823  
[Patent Document 3] JP-A-2001-121833  
[Patent Document 4] JP-A-2002-3665  
5 [Patent Document 5] Japanese Patent No.  
2846954

[Patent Document 6] Japanese Patent No.  
2846955

[Patent Document 7] JP-A-2003-526697

10 [Disclosure of Invention]

[Problem to be Solved by the Invention]

[0010]

It is an object of the present invention to provide a process for producing a printing original  
15 plate, which has a little amount of remaining organic compounds with unreacted polymerizable unsaturated groups in a cured photosensitive resin layer obtained by applying light, reduced hardness of the cured material and good laser engravability.

20 [Means for Solving the Problem]

[0011]

The present inventors have found that the problems described above can be solved by a process for producing a laser engravable flexographic printing  
25 original plate, characterized by comprising the steps of: forming a photosensitive resin composition layer on a cylindrical support or a sheeted support; applying light to the formed photosensitive layer to form a cured

laser engravable photosensitive resin layer; and then adjusting a thickness of the cured photosensitive resin layer and shaping the surface of the cured photosensitive resin layer, wherein the light applied to the photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter, and completed the present invention.

Also the method of the present invention is especially effective in forming a letterpress printing plate, where a large amount of sculpture debris is produced in forming the printing plate by removing the resin by applying laser light.

[0012]

The present invention is as follows.

1. A process for producing a laser engravable flexographic printing original plate, characterized by comprising the steps of: forming a photosensitive resin composition layer on a cylindrical support or a sheeted support; applying light to the formed photosensitive resin layer to form a cured laser engravable photosensitive resin layer; and then adjusting a thickness of the cured photosensitive resin layer and shaping a surface of the cured photosensitive resin

layer, wherein the light applied to the photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the photosensitive resin layer is 20  
5 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

[0013]

10 2. The process for producing a laser engravable flexographic printing original plate according to item 1, characterized by further comprising a step of applying light to the cured photosensitive resin layer again after the step of adjusting a thickness of the  
15 cured photosensitive resin layer and shaping a surface of the cured photosensitive resin layer, wherein the light again applied to the cured photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at  
20 a surface of the cured photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

25 [0014]

3. The process for producing a laser engravable flexographic printing original plate according to item 1 or 2, characterized in that the atmosphere in which the

light is applied to the photosensitive resin layer or the cured photosensitive resin layer is air.

4. The process for producing a laser engravable flexographic printing original plate according to item 5 1, 2 or 3, characterized in that the photosensitive resin layer is liquid at 20°C.

5. The process for producing a laser engravable flexographic printing original plate according to any of items from 1 to 4, characterized in that the 10 photosensitive resin layer and the cured photosensitive layer comprise an inorganic porous material (c).

6. The process for producing a laser engravable flexographic printing original plate according to any of items from 1 to 5, characterized in that the cured laser 15 engravable photosensitive resin layer is a seamless layer.

7. The process for producing a laser engravable flexographic printing original plate according to any of items from 1 to 6, characterized in that the 20 photosensitive resin composition comprises a photopolymerization initiator which contains a hydrogen extraction photopolymerization initiator and a collapse photopolymerization initiator.

[0015]

25 8. The process for producing a laser engravable flexographic printing original plate according to item 7, characterized in that the hydrogen extraction photopolymerization initiator comprises at least one



compounds selected from benzophenones, xanthenes and anthraquinones, and the collapse photopolymerization initiator comprises at least one compounds selected from benzoinalkyl ethers, 2,2-dialkoxy-2-phenyl

5 acetophenones, acyloxime esters, azo compounds, organic sulfur compounds and diketones.

[0016]

9. The process for producing a laser engravable flexographic printing original plate according to item 10 5, characterized in that the inorganic porous material (c) has an average pore diameter from 1 nm or more to 1000 nm or less, a pore volume from 0.1 ml/g or more to 10 ml/g or less, a specific surface area from 10 m<sup>2</sup>/g or more to 1500 m<sup>2</sup>/g or less and an oil absorption from 10 15 ml/100 g or more to 2000 ml/100g or less.

10. The process for producing a laser engravable flexographic printing original plate according to item 5 or 9, characterized in that the inorganic porous material (c) has a number average particle diameter from 20 0.1 μm or more to 100 μm or less, and at least 70% of the particles are spherical particles having a sphericity from 0.5 to 1.

[0017]

11. The process for producing a cylindrical laser 25 engravable flexographic printing original plate according to any of items from 1 to 10, characterized in that the photosensitive resin composition comprises a resin (a) having a number average molecular weight of

1000 or more and 200000 or less, an organic compound (b) having a number average molecular weight of less than 1000 and having a polymerizable unsaturated group in its molecule and an inorganic porous material (c).

5 12. The process for producing a cylindrical laser engravable flexographic printing original plate according to item 11, characterized in that 20 wt% or more of the total amount of the organic compound (b) is a derivative of at least one of alicyclic compounds or  
10 aromatic compounds.

[Advantages of the Invention]

[0018]

By the process for producing a printing original plate according to the present invention, a  
15 printing original plate is obtained, which has a little amount of remaining organic compounds with unreacted polymerizable unsaturated groups in the cured photosensitive resin layer obtained by applying light, reduced hardness of the cured material and a good laser  
20 engravability.

[Best Mode for Carrying Out the Invention]

[0019]

The present invention will be described in detail below focusing on its preferred embodiments.

25 A printing original plate of the present invention is a cylindrical laser engravable printing original plate. A part to which laser light is applied is removed to form a recessed portion.

A process for producing a laser engravable flexographic printing original plate according to the present invention comprises the steps of: forming a photosensitive resin composition layer on a cylindrical support or a sheeted support; applying light to the formed photosensitive resin layer to form a cured laser engravable photosensitive resin layer; and then adjusting a thickness of the cured photosensitive resin layer and shaping a surface of the cured photosensitive resin layer. Further, the process is characterized in that the light applied to the photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

[0020]

The present inventors have found a surprising effect in which by applying light having a high illuminance as described above, not only the curability of the inside and surface of the photosensitive resin composition layer can be ensured, but also the hardness of the obtained photo-cured material can be reduced. In the photosensitive resin composition, the increasing of the hardness of the photo-cured material can relatively easily be achieved, but it is extremely difficult to

shift the hardness to a lower level because it is necessary to considerably change the type of the polymer component or the organic compound having polymerizable unsaturated groups in the photosensitive resin composition used. The reason for this is that other properties such as the solvent resistance, the abrasion resistance and mechanical properties are often considerably degraded if components in the photosensitive resin composition are changed.

Therefore, the effect in which a reduction in hardness can easily be achieved by using a light source having a high illuminance was surprising. The result was also surprising that the reduction in hardness does not result from insufficient curing, namely, a large amount of the remaining unreacted polymerizable unsaturated groups in the photosensitive resin composition. The reason for this is presently unknown, but this is presumably because the mechanism of a reaction is considerably different for a case where the photo-curing reaction gradually proceeds by low-illuminance light and a case where the photo-curing reaction proceeds in a moment by very high-illuminance light. This phenomenon can be examined by an analytical method of heating the obtained photo-cured material at multiple steps of temperature using heat decomposition gas chromatography. That is, when a sample in a heat decomposition gas chromatographic apparatus is kept for a definite period of time at a temperature below the decomposition

temperature of a sample, unreacted organic compounds having polymerizable unsaturated groups vaporize out, and so this amount of the vaporized material can be quantitatively compared with by using gas chromatography.

[0021]

Further, a less amount of unreacted organic compounds having polymerizable unsaturated groups means a less amount of eluting components from the inside of the printing plate into the solvent used in printing, and this has an effect to reduce the changing over time of the printing plate used in printing.

The cured photosensitive resin obtained by very high-illuminance light has a less amount of liquid debris generated in laser engraving, and has an effect to inhibit the phenomenon that the dot patterns are made swollen and enlarged by the liquid debris generated.

Processes for forming a photosensitive resin composition layer on a cylindrical support or a sheeted support include, but are not specifically limited to, a process in which a liquid photosensitive resin composition is coated at 20°C, and a process in which a photosensitive resin composition that is solid at 20°C is heated and thereby melted, and extruded onto the support using an apparatus such as an extruder, and the thickness is formalized using a calendar roll or the like. For the process in which a liquid photosensitive resin composition is coated, a publicly known process

such as the doctor blade process, the spray coat process, the gravure coat process or the spin coat process may be employed.

[0022]

5           The formed photosensitive resin composition is crosslinked by application of light to form a laser engravable printing original plate. Furthermore, it may be crosslinked by application of light while it is molded. The process of crosslinking the photosensitive  
10 resin composition using light is suitable because it has an advantage that the apparatus is simple, the thickness accuracy can be improved, and so on. Light sources that are used for curing may include high-illuminance light sources such as metal halide lamps, high pressure  
15 mercury lamps, ultrahigh pressure mercury lamps, ultraviolet ray fluorescent lamps, carbon arc lamps and xenon lamps. Light from a plurality of types of light sources may be applied. However, even through a high-illuminance light source is used, the illuminance of  
20 light that is actually applied to the photosensitive resin composition layer is significantly influenced by the distance between the light source and the photosensitive resin composition layer and the presence of a light absorbing film or the like between the light  
25 source and the photosensitive resin composition layer, and therefore caution is required.

[0023]

In the present invention, a shaping step of

cutting, polishing and the like to obtain a predetermined thickness may be provided after coating a photosensitive resin composition layer on a support and photo-curing the photosensitive resin composition layer  
5 formed by applying high-illuminance light. It is more effective to apply high-illuminance light again after the shaping step to process the surface and the inside of the cured photosensitive resin layer.

In the present invention, the atmosphere in  
10 which light is applied to the photosensitive resin composition is preferably a gas atmosphere. Photo-curing in air is especially preferable, and the apparatus for use in application of light can further be simplified.

15 [0024]

Liquid debris generated in a laser engraving step can be absorbed away by including an inorganic porous material (c) in the cured laser engravable photosensitive resin layer. The photosensitive resin  
20 composition before being photo-cured preferably contains a resin (a) having a number average molecular weight of 1000 or more and 200000 or less, an organic compound (b) having a number average molecular weight of less than 1000 and having a polymerizable unsaturated group in its  
25 molecule, and an inorganic porous material (c).

[0025]

The type of the resin (a) may be an elastomer or a non-elastomer, and the resin may be a solid polymer

or a liquid polymer at 20°C. When a thermoplastic resin is used, it is contained in an amount of 30 wt% or more, preferably 50 wt% or more, further preferably 70 wt% or more of the total weight of the polymer. If the content of the thermoplastic resin is 30 wt% or more, the resin is sufficiently fluidized by application of a laser beam, and therefore absorbed by the inorganic porous material described later. If a resin of which the softening temperature is more than 300°C is used, there is the concern that other organic materials are degenerated or decomposed by heat because the temperature at which the resin is molded into a cylindrical shape becomes inevitably higher, and therefore a solvent-soluble resin is preferably coated and used in a state of being dissolved in a solvent.

[0026]

Particularly in terms of ease of processing into a cylindrical resin plate and ease of decomposition with heat, a polymer that is liquid at 20°C is preferably used as the resin (a). When a polymer that is liquid at 20°C is used as the resin (a), the formed photosensitive resin composition is also liquid, and therefore the resin can be molded at a low temperature.

The number average molecular weight of the resin (a) for use in the present invention is preferably in the range from 1000 to 200000. A more preferable is a range from 5000 to 100000. If the number average molecular weight is within the range from 1000 to



200000, the mechanical strength of the printing original plate can be ensured, and the resin can sufficiently be melted or decomposed during laser engraving. The number average molecular weight in the present invention is a value measured using gel permeation chromatography (GPC) and evaluated with reference to a polystyrene authentic sample of which the molecular weight is known.

[0027]

For the photosensitive resin used, a resin that is easily liquefied or easily decomposed is preferable. The resin that is easily decomposed preferably contains styrene,  $\alpha$ -methyl styrene,  $\alpha$ -methoxystyrene, acrylic esters, methacrylic esters, ester compounds, ether compounds, nitro compounds, carbonate compounds, carbamoyl compounds, hemiacetal ester compounds, oxyethylene compounds, aliphatic cyclic compounds or the like in a molecular chain as a monomer unit that is easily decomposed. Particularly, polyethers such as polyethylene glycol, polypropylene glycol and polytetraethylene glycol, aliphatic polycarbonates, aliphatic carbamates, polymethyl methacrylate, polystyrene, nitrocellulose, polyoxyethylene, polynorbornen, hydrogenated polycyclohexadienes, or polymers having a molecular structure such as a dendolymer having a large number of branched structures are typical examples of resins that are easily decomposed. Polymers containing a large number of oxygen atoms in a molecular chain are

preferable in terms of decomposability. Among them, compounds having a carbonate group, a carbamate group and a methacryl group in a polymer main chain have high heat decomposability and are therefore preferable. For example, polyesters and polyurethanes synthesized using (poly)carbonatediol and (poly)carbonate dicarboxylic acid as raw materials, and polyamides synthesized using (poly)carbonate diamine as a raw material may be listed as examples of polymers having good heat decomposability. Compounds containing polymerizable unsaturated groups in main chains and side chains of these polymers may be used. Particularly, if there is a reactive functional group such as a hydroxyl group, an amino group or a carboxyl group at the end, a polymerizable unsaturated group is easily introduced at the end of a main chain.

[0028]

Thermoplastic elastomers for use in the present invention may include, but are not specifically limited to, SBS (polystyrene-polybutadiene-polystyrene), SIS (polystyrene-polyisoprene-polystyrene), SEBS (polystyrene-polyethylene/polybutylene-polystyrene) and the like as styrene thermoplastic elastomers, olefin thermoplastic elastomers, urethane thermoplastic elastomers, ester thermoplastic elastomers, amide thermoplastic elastomers and silicone thermoplastic elastomers. A polymer having an easily decomposable functional group such as a highly decomposable carbamoyl

group or carbonate group introduced in a main chain in a molecular bone for further improving the heat decomposability may also be used.

[0029]

5                   The elastomer may be mixed with a polymer having higher heat decomposability and used. The thermoplastic elastomer is fluidized by heating, and therefore can be mixed with an organic porous material that is used in the present invention. The  
10 thermoplastic elastomer is a material which is fluidized by heating, can be molded and processed like a usual thermoplastic plastic, and shows rubber elasticity at normal temperature. A molecular structure consists of a soft segment such as a polyether or a rubber molecule  
15 and a hard segment preventing plastic deformation like a vulcanized rubber at near normal temperature, and for the hard segment, there are a variety of types such as a frozen phase, a crystalline phase, a hydrogen bond and an ion crosslink.

20 [0030]

                  The type of thermoplastic elastomer may be selected according to the application of the printing plate. For example, in a field where the solvent resistance is required, urethane, ester, amide and  
25 fluorine thermoplastic elastomers are preferable, and in a field where the heat resistance is required, urethane, olefin, ester and fluorine thermoplastic elastomers are preferable. The hardness can be varied greatly with the

type of thermoplastic elastomer. In the application for a usual printing plate, the Shore A hardness is in the range from 20 to 75 degrees, and in the application of embossing for forming surface concavo-convex patterns of papers, films and building materials, a relatively hard material is required, and in this case, the Shore D hardness is in the range from 30 to 80 degrees.

[0031]

Non-elastomer thermoplastic resins may include, but are not specifically limited to, polyester resins, unsaturated polyester resins, polyamide resins, polyamide imide resins, polyurethane resins, unsaturated polyurethane resins, polysulfone resins, polyethersulfone resins, polyimide resins, polycarbonate resins and fully aromatic polyester resins.

[0032]

The softening temperature of the thermoplastic resin of the present invention is preferably 50°C or more and 300°C or less. More preferable is a range from 80°C or more and 250°C or less, and further preferable is a range from 100°C or more and 200°C or less. If the softening temperature is 50°C or more, the resin can be handled as a solid at normal temperature, and the resin processed into a sheet shape or a cylindrical shape can be handled without being deformed. If the softening temperature is 300°C or less, it is not necessary to heat the resin to an extremely high temperature when processing the resin into a cylindrical shape, and

degradation or decomposition of other compounds mixed is thus avoided. For measurement of the softening temperature of the present invention, a dynamic viscoelasticity measuring apparatus is used, and the softening temperature is defined as an initial temperature at which the viscosity coefficient is sharply changed (the gradient of a viscosity coefficient curve is changed) when the temperature is elevated from room temperature.

10 [0033]

The resin (a) of the present invention may be a solvent-soluble resin. Specifically, solvent-soluble resins may include polysulfone resins, polyethersulfone resins, epoxy resins, alkyd resins, polyolefin resins and polyester resins.

Although most of the type of the resin (a) usually does not have highly reactive polymerizable unsaturated groups, the resin (a) of the present invention may have a polymerizable unsaturated group having a high reactivity at the end or side chain of the molecular chain. If a polymer having a polymerizable unsaturated group having a high reactivity is used, a printing original plate having an extremely high mechanical strength can be fabricated. Particularly, in the polyurethane and polyester thermoplastic elastomers, a polymerizable unsaturated group having a high reactivity can relatively easily be introduced to the inside of a molecule. The inside of a molecule

mentioned herein includes a case where a polymerizable unsaturated group is directly attached at the end of the polymer main chain, at the end of the polymer side chain, or in the polymer main or side chain, and so on.

5 For example, a resin having a polymerizable unsaturated group directly introduced at the end of the molecule may be used. But suitable alternative methods include a method in which a compound with a molecular weight of several thousands having a plurality of reactive groups  
10 such as hydroxide groups, amino groups, epoxy groups, carboxyl groups, acid anhydride groups, ketone groups, hydrazine groups, isocyanate groups, isothiocyanate groups, cyclic carbonate groups, ester groups and the like are reacted with a binder (e.g. polyisocyanate in  
15 the case of hydroxyl groups and amino groups) having a plurality of groups capable of binding to the reactive group of the compound, and after adjustment of the molecular weight and conversion into a binding group at the end are carried out, the reaction product is then  
20 reacted with an organic compound having a group reacting with this binding group at the end and a polymerizable unsaturated group to introduce the polymerizable unsaturated group at the end.

[0034]

25           The organic compound (b) is a compound having an unsaturated bond involved in a radical or addition polymerization reaction, and its number average molecular weight is preferably less than 1000 in

consideration of ease of dilution with the resin (a).  
Functional groups having an unsaturated bond involved in  
the radical polymerization reaction include a vinyl  
group, an acetylene group, an acryl group, a methacryl  
5 group and an allyl group as preferable examples.

Functional groups having an unsaturated bond involved in  
the addition polymerization reaction may include a  
cynnamoil group, a thiol group, an azido group, an epoxy  
group that undergoes a ring-opening addition reaction,  
10 an oxethane group, a cyclic ester group, a dioxilane  
group, a spiroortho carbonate group, a spiroortho ester  
group, bicycloortho ester group, a cyclosiloxane group  
and a cyclic iminoether group.

[0035]

15                Specific examples of the organic compound (b)  
include olefins such as ethylene, propylene, styrene and  
divinyl benzene, acetylenes, (meta)acrylic acids and  
derivatives thereof, haloorefins, unsaturated nitriles  
such as acrylonitrile, (meta)acryl amides and  
20 derivatives thereof, allyl compounds such as allyl  
alcohol and allyl isocyanate, unsaturated dicarboxylic  
acids such as maleic anhydride, maleic acid and fumaric  
acid and derivatives thereof, vinyl acetates, N-vinyl  
pyrrolidone and N-vinylcarbazole. (Meta)acrylic acids  
25 and derivatives thereof are preferable examples in terms  
of abundance in the type, the price, decomposability  
during application of laser light, and so forth. The  
derivatives of the compounds include alicyclic compounds

having a cycloalkyl group, a bicycloalkyl group, a cycloalkene group, a bicycloalkene group and the like, aromatic compounds having a benzyl group, a phenyl group, a phenoxy group, a fluorene group and the like,  
5 and esters of polyhydric alcohols having an alkyl group, a halogenated alkyl group, an alkoxy alkyl group, a hydroxy alkyl group, an amino alkyl group, a tetrahydrofurfuryl group, allyl group, a glycidyl group, alkylene glycol group, polyoxyalkylene glycol group,  
10 (alkyl/aryl)polyalkylene glycol group, trimethylolpropane group and the like. Heterocyclic aromatic compounds having an element such as nitrogen or sulfur may be included.

[0036]

15               Compounds having an epoxy group that undergoes a ring-opening addition reaction may include compounds obtained from epichloro hydrin reacted with various kinds of polyols such as diol and triol, and epoxy compounds obtained from an ethylene bond in a molecule  
20 reacted with a peracid. Specific examples include ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, triethylene glycol diglycidyl ether, tetraethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl  
25 ether, tripropylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin diglycidyl ether, glycerin triglycidyl ether,



trimethylol propane triglycidyl ether, Bisphenol A diglycidyl ether, hydrogenated Bisphenol A diglycidyl ether, diglycidyl ethers of addition compounds of Bisphenol A with ethylene oxide or propylene oxide,  
5 polytetramethylene glycol diglycidyl ether, poly(propylene glycol adipate)diol diglycidyl ether, poly(ethylene glycol adipate)diol diglycidyl ether and poly(caprolactone)diol diglycidyl ether.

[0037]

10 In the present invention, one or more types of organic compounds (b) having these polymerizable unsaturated bonds may be selected according to the purpose thereof. For example, if the compound is used for a printing plate, at least one type of long-chain  
15 aliphatic, alicyclic or aromatic derivative is preferably included as the organic compound (b) which suppresses swelling by an organic solvent such as an alcohol or an ester that is used as a solvent for a printing ink.

20 [0038]

For improving the mechanical strength of printing original plate obtained from the resin composition of the present invention, at least one type of alicyclic or aromatic derivatives is preferably  
25 included as the organic compound (b). In this case, the amount of the derivative is preferably 20 wt% or more, further preferably 50 wt% or more based on the total amount of organic compound (b). The aromatic derivative

may be an aromatic compound having elements such as nitrogen and sulfur.

For improving the rebound resilience of the printing plate, a methacryl monomer described in, for example, JP-A-7-239548 may be used, or a selection may be made using technical information of publicly known photosensitive resins for printing, and so forth.

[0039]

The inorganic porous material (c) is inorganic particles having very small pores or very small air gaps in particles. The inorganic porous material (c) is an additive for absorbing away sticky liquid debris generated in a large amount in laser engraving, and also has an effect of preventing tack on the plate surface. In addition to the requirement that it should not be melted by laser application, the quality is not specifically limited, but when photo-curing is performed using an ultraviolet ray or a visible light ray, the transmittance of light into the photosensitive resin composition considerably decreases to cause a degradation in properties of the cured material if black fine particles are added, and therefore black fine particles such as carbon black, activated carbon and graphite are not suitable as the inorganic porous material (c) of the present invention.

[0040]

The pore volume of the inorganic porous material (c) is preferably 0.1 ml/g or more and 10 ml/g

or less, more preferably 0.2 ml/g or more and 5 ml/g or less. If the pore volume is 0.1 m/g or more, the absorption of sticky liquid debris is sufficient, and if the pore volume is 10 ml/g or less, the mechanical  
5 strength of particles can be ensured. In the present invention, a nitrogen absorption method is used for measurement of the pore volume. The pore volume in the present invention is determined from an absorption isotherm of nitrogen at -196°C.

10 [0041]

The average pore diameter of the inorganic porous material (c) very greatly influences the absorption of liquid debris generated during laser engraving. The range of the average pore diameter is  
15 preferably from 1 nm or more to 1000 nm or less, more preferably from 2 nm or more to 200 nm or less, further preferably from 2 nm or more to 50 nm or less. If the average pore diameter is 1 nm or more, the absorption of liquid debris generated during laser engraving can be  
20 ensured, and if the average pore diameter is 1000 nm or less, the specific surface areas of particles are so large that the absorption of liquid debris can sufficiently be ensured. The reason why the absorption of liquid debris is low if the average pore diameter is  
25 less than 1 nm has not been clarified, but it can be assumed that liquid debris is sticky and therefore hard to enter a micropore. The average pore diameter of the present invention is a value measured using a nitrogen

adsorption method. Pores having an average pore diameter of 2 to 50 nm are particularly called mesopores, and porous particles having mesopores have an extremely high capability of absorbing liquid debris.

- 5 The pore diameter distribution in the present invention is determined from an absorption isotherm of nitrogen at -196°C.

[0042]

- The present invention has the most striking
- 10 characteristic in introduction of a new concept absent in previous technological ideas that a resin having a relatively low molecular weight is employed so that it is easily cut preferably by application of a laser, and resultantly, low-molecular weight monomers and oligomers
- 15 are generated in a large amount when molecules are cut, and therefore this sticky liquid debris is removed using a porous inorganic absorbent. For effectively removing sticky liquid debris, the properties such as the number average particle diameter, the specific surface area,
- 20 the average pore diameter, the pore volume, the ignition loss and the oil absorption of the inorganic porous material are important factors.

[0043]

- The inorganic porous material (c) preferably
- 25 has a number average particle diameter of 0.1 to 100  $\mu\text{m}$ . If an inorganic porous material having a number average particle diameter below this range is used, powder dust tends to fly to contaminate a sculpture apparatus when

an original plate obtained from the resin composition of the present invention is sculptured, and in addition, a rise in viscosity, entanglement of air bubbles and generation of powder dust tend to occur when the

5 inorganic porous material is mixed with the resin (a) and the organic compound (b). If an inorganic porous material having a number average particle diameter above the aforementioned range is used, defects tend to occur in relief images at the time of laser engraving, and the

10 fineness of printed matters tends to be impaired. A more preferable range of the average particle diameter is from 0.5 to 20  $\mu\text{m}$ , and a further preferable range is from 3 to 10  $\mu\text{m}$ . The average particle diameter of the inorganic porous material for use in the present

15 invention can be measured using a laser scattering particle diameter distribution measuring apparatus.

[0044]

A new concept of a degree of porosity is introduced in evaluation of properties of the porous

20 material. The degree of porosity is defined by a ratio of a specific surface area  $P$  to a surface area  $S$  per unit weight that is calculated from an average particle diameter  $D$  (unit:  $\mu\text{m}$ ) and a density  $d$  (unit:  $\text{g}/\text{cm}^3$ ) of a material forming particles, namely  $P/S$ . Since the

25 surface area per particle is  $\pi D^2 \times 10^{-12}$  (unit:  $\text{m}^2$ ) and the weight per particle is  $(\pi D^3 d / 6) \times 10^{-12}$  (unit:  $\text{g}$ ), the surface area  $S$  per unit weight is  $S = 6 / (Dd)$  (unit:  $\text{m}^2/\text{g}$ ). For the specific surface area  $P$ , a value measured

with nitrogen molecules adsorbed to the surface is used.  
[0045]

The degree of porosity of the inorganic porous material (c) is preferably 20 or more, more preferably 50 or more, further preferably 100 or more. If the degree of porosity is 20 or more, liquid debris is effectively absorbed away. Since the specific surface area  $P$  increases as the particle diameter decreases, the specific area alone is not suitable as an index showing the properties of the porous material. Therefore, the degree of porosity is employed as an index which is made dimensionless considering the particle diameter. For example, carbon black that is widely used as a reinforcement material for rubber and the like has a very large specific surface area of  $150 \text{ m}^2/\text{g}$  to  $20 \text{ m}^2/\text{g}$  but has an extremely small average particle diameter which is usually 10 nm to 100 nm, and therefore when the degree of porosity is calculated provided that the density is  $2.25 \text{ g/cm}^3$  for graphite, the obtained value is in a range from 0.8 to 1.0, and carbon black is presumed to be a nonporous material having no porous structures in particles. Since carbon black is generally known to have a graphite structure, a value for graphite is used for the density. The degree of porosity of porous silica that is used in the present invention has a high value well exceeding 500.

[0046]

The inorganic porous material of the present

invention preferably has a specified specific surface area and oil absorption for obtaining a further satisfactory absorption.

The range of the specific surface area of the inorganic porous material (c) is preferably from 10 m<sup>2</sup>/g or more and 1500 m<sup>2</sup>/g or less, more preferably from 100 m<sup>2</sup>/g or more and 800 m<sup>2</sup>/g or less. If the specific surface area is 10 m<sup>2</sup>/g or more, removal of liquid debris during laser engraving is sufficient, and if the specific surface area is 1500 m<sup>2</sup>/g or less, a rise in viscosity of the photosensitive resin composition can be inhibited and thixotropy can be inhibited. The specific surface area in the present invention is determined based on the BET equation from an absorption isotherm of nitrogen at -196°C.

[0047]

There is an oil absorption as an index for evaluating the absorption of liquid debris. This is defined by the amount of oil absorbed by 100 g of inorganic porous material. The range of the oil absorption of the inorganic porous material for use in the present invention is preferably from 10 ml/100 g or more to 2000 ml/100 g or less, more preferably from 50 ml/100 g or more to 1000 ml/100 g or less, further preferably from 200 ml/100 g or more to 800 ml/100 g or less. If the oil absorption is 10 ml/100 g or more, liquid debris generated during laser engraving is effectively removed, and if the oil absorption is 2000

ml/100 g or less, the mechanical strength of the inorganic porous material can sufficiently be ensured. The measurement of the oil absorption is preferably carried out in accordance with JIS-K5101.

5 [0048]

The inorganic porous material (c) of the present invention preferably retains porosity without being deformed or melted by application of laser light particularly in an infrared wavelength range. The  
10 ignition loss after processing at 950°C for 2 hours is preferably 15 wt% or less, more preferably 10 wt% or less.

The shape of particles of the inorganic porous material is not specifically limited, and spherical  
15 particles, flat particles, acicular particles, amorphous particles, particles having projections on the surfaces, or the like may be used. Among them, spherical particles are especially preferable in terms of the abrasion resistance of the printing plate. HOLLOWED  
20 particles, spherical granules having uniform pore diameters, such as a silica sponge, and the like can also be used. Examples thereof may include, but are not specifically limited to, porous silica, mesoporous silica, silica-zirconia porous gel, mesoporous molecular  
25 sieve, porous alumina and porous glass.

[0049]

For materials having air gaps of several nm to 100 nm between layers, such as layered clay compounds,



the pore diameter cannot be defined, and therefore air gaps existing between layers, namely face intervals are defined as a pore diameter. The total amount of spaces existing between layers is defined as a pore volume.

- 5 These values can be determined from the absorption isotherm of nitrogen.

Further, an organic coloring matter such as a pigment or a dye absorbing light having a wavelength of laser light can be captured in these pores or air gaps.

10 [0050]

The sphericity is defined as an index for specifying spherical particles. The sphericity for use in the present invention is defined by a ratio of a maximum value  $D_1$  of a circle fully encompassing the  
15 projected view to a minimum value  $D_2$  of a circle fully encompassing the projected view,  $(D_1/D_2)$  when particles are projected. In the case of a sphere, the sphericity is 1.0. The sphericity of spherical particles for use in the present invention is preferably 0.5 or more and  
20 1.0 or less, more preferably 0.7 or more and 1.0 or less. If the sphericity is 0.5 or more, the abrasion resistance as a printing plate is satisfactory. The sphericity of 1.0 is an upper limit of the sphericity. As spherical particles, 70% or more, more preferably 90%  
25 or more of particles desirably have a sphericity of 0.5 or more. As a method for measuring the sphericity, a method in which the sphericity is measured based on a photograph taken using a scanning electron microscope

may be used. At this time, a photograph is preferably taken under a magnification allowing at least 100 particles to be encompassed within a monitor screen. The above described  $D_1$  and  $D_2$  are measured based on a  
5 photograph, but preferably, the photograph is processed using an apparatus such as a scanner for digitizing the photograph, and data is then processed using image analysis software.

[0051]

10 The surface of the inorganic porous material may be coated with a silane coupling agent, titanium coupling agent or other organic compound to perform a surface modification treatment to use more hydrophilic or hydrophobic particles.

15 In the present invention, one or more types of the inorganic porous material (c) may be selected, and by adding the inorganic porous material (c), generation of liquid debris during laser engraving is inhibited and tacks and the like on the relief printing plate are  
20 improved effectively.

[0052]

In showing the fractions of the resin (a), the organic compound (b) and the inorganic porous material (c) in the photosensitive resin composition of the  
25 present invention, usually, the amount of organic compound (b) is preferably in a range from 5 to 200 parts by weight, more preferably in a range from 20 to 100 parts by weight based on 100 parts by weight of

resin (a). The amount of inorganic porous material (c) is preferably in a range from 1 to 100 parts by weight, more preferably in a range from 2 to 50 parts by weight, further preferably in a range from 2 to 20 parts by weight based on 100 parts by weight of resin (a).

If the ratio of the organic compound (b) is within the aforementioned range, the hardness and the tensile strength elongation are easily balanced, shrinkage in crosslinkage curing is reduced, and the thickness accuracy can be ensured.

[0053]

If the amount of inorganic porous material (c) is within the aforementioned range, the effect of preventing tacks on the surface of the plate and the effect of inhibiting generation of sculpture liquid debris at the time of laser engraving are sufficiently exhibited, the mechanical strength of the printing plate can be ensured, and the transparency can be retained. When the inorganic porous material (c) is used for a flexographic plate, the hardness can be controlled so as not to be too high. When the photosensitive resin composition is cured using light, especially ultraviolet light, to fabricate a laser engraving printing original plate, the light transmission property influences a curing reaction. Thus, it is effective to use an inorganic porous material having a refractive index close to that of the photosensitive resin composition.

[0054]

The photosensitive resin composition of the present invention is crosslinked by application of light or an electron beam to realize properties as a printing plate or the like, and at this time, a polymerization  
5 initiator may be added. The polymerization initiator may be selected from those that are generally used, and for example, initiators for radical polymerization, cationic polymerization and anionic polymerization illustrated in "Polymer Data Handbook - Basic Part"  
10 edited by The Society of Polymer Science, Japan; published by BAIFUKAN CO., LTD., 1986, may be used. Crosslinking the resin composition by photopolymerization using a photopolymerization initiator is useful as a method allowing printing  
15 original plates to be produced with good productivity while maintaining the storage stability of the resin composition of the present invention, and a publicly known initiator may be used as an initiator that is used in this case. For the photopolymerization initiator  
20 inducing a radical polymerization reaction, hydrogen extraction photopolymerization initiators and collapse photopolymerization initiators are widely used as especially effective photopolymerization initiators. For photo-curing in air, it is especially preferable  
25 that a hydrogen extraction photopolymerization initiator and a collapse photopolymerization initiator are used in combination.

[0055]

The hydrogen extraction polymerization initiator is not specifically limited, but aromatic ketone is preferably used. Aromatic ketone goes into an excitation triplet state efficiently by optical

5 excitation, and for this excitation triplet state, a chemical reaction mechanism in which hydrogen is extracted from surrounding media to generate radicals has been proposed. It is conceivable that the generated radicals are involved in a photo-crosslinking reaction.

10 The hydrogen extraction photopolymerization initiator for use in the present invention may be any compound as long as it extracts hydrogen from surrounding media to generate radicals via the excitation triplet state. Aromatic ketones may include benzophenones, Michler's

15 ketones, xanthenes, thioxanthenes and anthraquinones, and at least one type of compound selected from the group consisting of these compounds is preferably used. Benzophenones refer to benzophenone and derivatives thereof, specific examples of which include 3,3',4,4'-

20 benzophenonetetracarboxylic anhydride and 3,3',4,4'-tetramethoxybenzophenone. Michler's ketones refer to Michler's ketone and derivatives thereof. Xanthenes refer to xanthene and derivatives substituted with an alkyl group, a phenyl group and a halogen group.

25 Thioxanthenes refer to thioxanthone and derivatives substituted with an alkyl group, a phenyl group and a halogen group, which may include ethylthioxanthone, methylthioxanthone and chlorothioxanthone.

Anthraquinones refer to anthraquinone and derivatives substituted with an alkyl group, a phenyl group, a halogen group and the like. The added amount of hydrogen extraction photopolymerization initiator is preferably 0.1 wt% or more and 10 wt% or less, more preferably 0.5 wt% or more and 5 wt% or less of the total amount of photosensitive resin composition. If the added amount is within this range, the curability of the surface of the cured material can sufficiently be ensured and the weather resistance can be ensured when a liquid photosensitive resin composition is photo-cured in air.

[0056]

The collapse photopolymerization initiator refers to a compound in which after absorption of light, a cleavage reaction occurs in a molecule and active radicals are generated, and is not specifically limited. Specific examples thereof may include benzoinalkyl ethers, 2,2-dialkoxy-2-phenyl acetophenones, acetophenones, acyloxime esters, azo compounds, organic sulfur compounds and diketones, and at least one compound selected from the group consisting of these compounds is preferably used. Benzoinalkyl ethers may include benzoinisopropyl ether, benzoinisobutyl ether, and compounds described in "Photosensitive Polymers" (Kodansha Co., Ltd., published in 1977, p. 228). 2,2-dialkoxy-2-phenyl acetophenones may include 2,2-dimethoxy-2-phenyl acetophenone and 2,2-diethoxy-2-

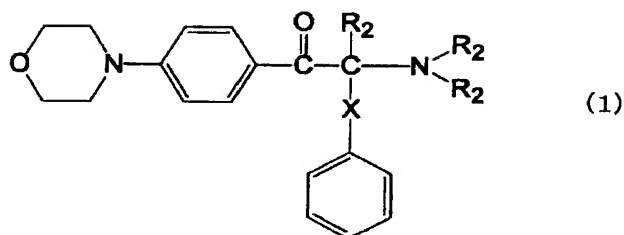
phenyl acetophenone. Acetophenones may include acetophenone, trichloro acetophenone, 1-hydroxycyclohexylphenyl acetophenone and 2,2-diethoxy acetophenone. Acyloxime esters may include 1-phenyl-  
5 1,2-propanedione-2-(o-benzoyl)oxime. Azo compounds may include azobis isobutyronitorile, diazonium compounds and tetrazene compounds. Organic sulfur compounds may include aromatic thiol, mono and disulfide, thiuram sulfide, dithiocarbamate, S-acyl dithiocarbamate,  
10 thiosulfonate, sulfoxide, sulphenate and dithiocarbonate. Diketones may include benzyl and methyl benzoyl formate. The added amount of collapse photopolymerization initiator is preferably 0.1 wt% or more and 10 wt% or less, more preferably 0.3 wt% or more  
15 and 3 wt% or less of the total amount of the photosensitive resin composition. If the added amount is within this range, the curability of the inside of the cured material can sufficiently be ensured when the photosensitive resin composition is photo-cured in air.  
20 [0057]

A compound having in the same molecule a site functioning as the hydrogen extraction photopolymerization initiator and a site functioning as the collapse photopolymerization initiator may also be  
25 used as a photopolymerization initiator. Examples thereof may include  $\alpha$ -aminoacetophenones. They may include, for example, 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propan-1-one and compounds expressed by the

general formula (1).

[0058]

[Formula 1]



[0059]

5 (In the formula, R<sub>2</sub> each independently represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms. X represents an alkylene group having 1 to 10 carbon atoms.)

[0060]

10 The added amount of the compound having in the same molecule a site functioning as the hydrogen extraction photopolymerization initiator and a site functioning as the collapse photopolymerization initiator is preferably 0.1 wt% or more and 10 wt% or  
15 less, more preferably 0.3 wt% or more and 3 wt% or less of the total amount of the photosensitive resin composition. If the added amount is within this range, the mechanical properties of the cured material can sufficiently be ensured even when the photosensitive  
20 resin composition is photo-cured in air.

[0061]

A photopolymerization initiator inducing an



addition polymerization reaction by absorbing light and generating an acid may also be used. Examples of the photopolymerization initiator include photo-cationic polymerization initiators such as aromatic diazonium salts, aromatic iodonium salts and aromatic sulfonium salts, or polymerization initiators absorbing light and generating a base. The added amount of the photopolymerization initiator is preferably in a range from 0.1 wt% or more and 10 wt% or less of the total amount of photosensitive resin composition.

In addition, to the resin composition of the present invention may be added a polymerization inhibitor, an ultraviolet absorbing agent, a dye, a pigment, a lubricant, a surfactant, a plasticizer, a flavor and the like may be added according to the application and purpose.

[0062]

For the method for molding the photosensitive resin composition of the present invention into a cylindrical shape, an existing method for molding resins may be used. Examples of the method may include a cast molding method, and a method in which a resin is extruded from nozzles or dies by a machine such as a pump or an extruder, and calendered by a roll for making the thickness uniform by a blade to make the thickness uniform. In this case, it is also possible to carry out molding while heating the resin within the bounds not degrading the performance of the resin. The resin may

also be subjected to rolling, grinding and the like as necessary. Furthermore, a printing plate can be formed using a cylindrical printing original plate formation/sculpture apparatus having a laser light source for laser engraving incorporated in an apparatus for curing/solidifying a photosensitive resin composition by applying light after coating the photosensitive resin composition on a cylindrical support. If such an apparatus is used, laser engraving can be carried out to form a printing plate just after forming a cylindrical printing original plate, thus making it possible to realize short-time processing far beyond what can be conceived for a conventional rubber sleeve requiring a period of several weeks for molding. In a step of fabricating a cylindrical printing original plate, the cylindrical printing original plate can be fabricated in an extremely short time by using the photosensitive resin composition.

[0063]

The cylindrical support for use in the present invention may be rigid or flexible. It may also be sheeted support. The role of the support for use in the present invention is to ensure the dimensional stability of the printing original plate. Thus, a support having high dimensional stability is preferably selected. When an evaluation is made using a linear expansion coefficient, the upper limit for a preferable material is 100 ppm/°C or less, further preferably 70 ppm/°C or

less. Specific examples of the material may include polyester resins, polyimide resins, polyamide resins, polyamide imide resins, polyether imide resins, polybismaleimide resins, polysulfone resins, polycarbonate resins, polyphenylene ether resins, polyphenylene thioether resins, polyether sulfone resins, liquid crystal resins composed of fully aromatic polyester resins, fully aromatic polyamide resins, epoxy resins and metals. These resins may also be laminated and used.

[0064]

Methods for reducing the linear expansion coefficient of the support may include a method in which a filler is added, and a method in which a meshed cloth of fully aromatic polyamide or the like, a glass cloth, or the like is impregnated or coated with a resin. For the filler, organic fine particles that are usually used, inorganic fine particles such as metal oxides or metals, organic/inorganic composite fine particles and the like may be used. Porous fine particles, hollowed fine particles, microcapsule particles, and layered compound particles with a low-molecular compound intercalated therein may also be used. Particularly, fine particles of metal oxides such as alumina, silica, titanium oxide and zeolite, latex fine particles composed of a polystyrene/butadiene copolymer, organic fine particles and fibers of natural products such as highly crystalline celluloses and highly crystalline

cellulose nanofibers produced by organisms, and the like are useful. Materials such as fiber reinforcement plastics (FRP) are especially useful for the cylindrical support.

5 [0065]

By chemically and physically treating the surface of the cylindrical or sheeted support for use in the present invention, the adhesion of the support with a cushion layer can be improved. Physical treatment  
10 methods may include a sand blast method, a wet blast method of jetting a liquid containing fine particles, a corona discharge treatment method, a plasma treatment method, and an ultraviolet ray or vacuum ultraviolet ray irradiation method. Chemical treatment methods include  
15 a strong acid/strong alkali treatment method, an oxidant treatment method and a coupling treatment method.

The thickness of the cured laser engravable photosensitive resin layer may freely be set according to the purpose of use, but it is generally in a range  
20 from 0.1 to 7 mm when the cured photosensitive resin layer is used for a printing plate. In some cases, a plurality of materials having different compositions may be laminated.

[0066]

25 The laser engravable printing original plate of the present invention is preferably a printing original plate formed by photo-crosslinking and curing a photosensitive material containing inorganic porous

material fine particles. Thus, a three-dimensionally crosslinked structure is formed by a reaction of a polymerizable unsaturated group of the organic compound (b) or by reaction of a polymer with the polymerizable unsaturated group of the organic compound (b), and the photosensitive material becomes insoluble in ester, ketone, aromatic, ether, alcohol and halogen solvents that are usually used. This reaction occurs between organic compounds (b), between resins (a) or between the resin (a) and the organic compound (b), and the polymerizable unsaturated group is consumed. When the photosensitive material is crosslinked and cured using a photopolymerization initiator, the photopolymerization initiator is decomposed by light, and therefore an unreacted photopolymerization initiator and a decomposition product can be identified by extracting the crosslinked and cured material with a solvent and performing analysis using the GC-MS method (method of performing mass analysis of a substance separated by gas chromatography), the LC-MS method (method of performing mass analysis of a substance separated by liquid chromatography), the GPS-MS method (method of separating a substance by gel permeation chromatography and performing mass analysis of the substance) or the LC-NMR method (method of separating a substance by a liquid chromatography and performing analysis of the substance by a nuclear magnetic resonance spectrum. Further, by using the GPC-MS method, the LC-MS method or the GPC-NMR

method, an unreacted resin (a), an unreacted organic compound (b) and a relatively low molecular weight product obtained by a reaction of a polymerizable unsaturated group in a solvent extracted material can be  
5 identified from analysis of the solvent extracted material. For solvent-insoluble high molecular weight components forming the three-dimensionally crosslinked structure, whether a site generated by the reaction of the polymerizable unsaturated group is present as a  
10 component forming the high molecular weight material can be verified by using the pyrolysis GC-MS method. For example, the presence of a site by the reaction of a polymerizable unsaturated group such as a methacrylate group, an acrylate group or a vinyl group can be  
15 predicted from a mass analysis spectrum pattern. The pyrolysis GC-MS method is a method in which a sample is decomposed by heating, generated gas components are separated by gas chromatography, and mass analysis is then performed. If a decomposition product originating  
20 from the photopolymerization initiator or an unreacted photopolymerization initiator is detected together with an unreacted polymerizable unsaturated group or a site obtained by the reaction of the polymerizable unsaturated group in the crosslinked and cured material,  
25 it can be concluded that this material has been obtained by photo-crosslinking and curing the photosensitive resin composition.

[0067]

The amount of inorganic porous material fine particles present in the crosslinked and cured material can be obtained by heating the crosslinked and cured material in air to burn off organic components and  
5 measuring the weight of residues.

The presence of inorganic porous material fine particles in the residues can be identified from observation of the morphology by a field emission high-resolution scanning electron microscope, and  
10 measurements of a particle diameter distribution by a laser scattering particle diameter distribution measuring apparatus and a pore volume, a pore diameter distribution and a specific surface area by a nitrogen adsorption method.

15 [0068]

In laser engraving, a laser apparatus is operated using a computer with an image to be formed as digital data, and a relief image is created on an original plate. The laser for use in laser engraving  
20 may be any laser as long as it includes a wavelength at which the original plate has an absorption. For performing sculpture at a high speed, a laser having a high output is desirable, and a laser having an oscillation wavelength in an infrared or near-infrared  
25 range, such as a carbon dioxide laser, a YAG laser, a semiconductor laser or a fiber laser, is one of preferable lasers. An ultraviolet laser having an oscillation wavelength in an ultraviolet range, for

example an excimer laser, a YAG laser having a wavelength converted to a third or fourth high harmonic wave, a copper vapor laser or the like is capable of abrasion processing to cut a bond of organic molecules, and is suitable for microprocessing. A laser having an extremely high peak output, such as a femto-second laser, may also be used. The laser may be a continuous irradiation laser or a pulse irradiation laser. The resin generally has an absorption at near about 10  $\mu\text{m}$ , i.e. the oscillation wavelength of the carbon dioxide gas laser, and therefore it is not particular necessary to add a component to help absorption of laser light. The YAG laser, the semiconductor laser and the fiber laser have an oscillation wavelength at near 1  $\mu\text{m}$ , but there are not so many organic materials having an optical absorption in this wavelength range. In this case, addition of a dye or a pigment which is a component to help the absorption is required. Examples of such dyes include poly (substituted) phthalocyanine compounds and metal-containing phthalocyanine compounds; cyanine compounds; squarrium dyes; chalcogenopyrilo allylidene dyes; chloronium dyes; metal thiolated dyes; bis(chalcogenopyrilo)polymethine dyes; oxyindolizine dyes; bis(aminoaryl)polymethine dyes; melocyanine dyes; and quinoide dyes. Examples of pigments include dark-color inorganic pigments such as carbon black, graphite copper chromite, chrome oxide, cobalt chrome aluminate and iron oxide, metal powders of iron, aluminum, copper,



zinc and the like, and these metals doped with Si, Mg, P, Co, Ni, Y and the like. These dyes and pigments may be used alone, or may be used in combination of two or more types, or may be combined in any form such as a  
5 multilayered structure. However, when the photosensitive resin composition is cured using an ultraviolet ray or a visible light ray, the added amount of coloring matter or pigment having an absorption in a light ray range used is preferably limited to a low  
10 level for curing the printing original plate to its inside.

[0069]

Sculpture with a laser is carried out under an oxygen-containing gas, generally under the presence of  
15 air or air stream, but may be carried out under carbon dioxide gas or nitrogen gas. Powdered or liquid materials emerging in a slight amount on the surface of a relief printing plate after completion of sculpture may be removed using an appropriated method, for example  
20 a method in which the materials are washed out with a solvent, water containing a surfactant, or the like, a method in which an aqueous cleaner is jetted by a high-pressure spray or the like, or a method in which high-pressure steam is jetted.

25 The original plate produced according to the present invention can be applied and used for relief images for a printing plate as well as for various kinds of applications such as stamps/seals, design rolls for

embossing, relief images for the patterning of insulator, resistor and conductor pastes that are used for fabrication of electronic components, relief images for mold materials of ceramic products, relief images  
5 for displays such as advertisement/display boards, and molds/matrixes of various kinds of molded products.

[Examples]

[0070]

The present invention will be described based  
10 on examples, but the present invention is not limited to these examples.

In Examples and Comparative Examples, laser engraving was carried out using a carbon dioxide gas sculpture machine (trade mark "ZED-mini-1000"  
15 manufactured by ZED Co., Ltd. (United Kingdom), and for patterns of sculpture, patterns including dots, line drawings by salient lines having a width of 500  $\mu\text{m}$ , and void lines having a width of 500  $\mu\text{m}$  were created. Since the area of the top part of fine dot portion patterns  
20 cannot be ensured and the patterns get out of shape and become unclear if the sculpture depth is set to be large, the sculpture depth was set to 0.55 mm.

[0071]

After laser engraving, debris on the relief  
25 printing plate was wiped off using a nonwoven fabric (trade mark "BEMCOT M-3" manufactured by Asahi Chemical Industry Co., Ltd.) impregnated with ethanol or acetone. The weights of the printing original plate before laser

engraving, the printing plate just after laser engraving and the relief printing plate just after wiping off debris were measured, and the residual ratio of debris during sculpture was determined according to the  
5 following formula.

(weight of plate just after sculpture - weight of plate after wiping off debris) ÷ (weight of original plate before sculpture - weight of plate after wiping off debris) × 100

10 [0072]

Measurement of tacks on the surface of the relief printing plate after wiping off debris was carried out using Tack Tester manufactured by Toyo Seiki Seisaku-Sho, Ltd. For the measurement of tacks, a part  
15 of 13 mm width of an aluminum ring having a radius of 50 mm and a width of 13 mm is brought into contact with a flat part of a sample piece at 20°C, a load of 0.5 kg is imposed on the aluminum ring, the aluminum ring is left standing for 4 seconds, the aluminum ring is then lifted  
20 at a constant speed of 30 mm per minute, and a resistance force when the aluminum ring departs from the sample piece is read with a push pull gage. As this value increases, the tackiness degree increases and the adhesive strength becomes higher.

25 Further, the shape of a dot portion having an area ratio of about 10% at 80 lpi (lines per inch) among sculpted parts was observed with an electron microscope.

For the measurement of the specific surface

area of fine particles and the pore distribution, measurements were made by adsorption of nitrogen gas under an atmosphere of the liquid nitrogen temperature using AUTOSOAP 3MP manufactured by Quantachrome Corporation (United States).

[0073]

As the resin (a), resins (a1) to (a3) were produced in Production Examples 1 to 3 described below. (Production Example 1)

10 To a 1L separable flask having a thermometer, a stirrer and a circulator were added 447.24 g of polycarbonate diol (trade mark "PCDL L4672" (number average molecular weight: 1990; and OH value: 56.4) manufactured by Asahi Chemical Industry Co., Ltd.) and  
15 30.83 g of tolylene diisocyanate, the mixture was allowed to react for about 3 hours under heating at 80°C, 14.83 g of 2-methacryloyl oxyisocyanate was then added, and the mixture was further allowed to react for about 3 hours to produce a resin (a1) having a methacryl group  
20 (having about two intramolecular polymerizable unsaturated groups per molecule on the average) at the end and having a number average molecular weight of about 10000. This resin was in the form of thick malt syrup at 20°C, was fluidized when applying an external  
25 force, and did not recover its original shape even when removing the external force.

[0074]

(Production Example 2)

To a 1L separable flask having a thermometer,  
a stirrer and a circulator were added 447.24 g of  
polycarbonate diol (trade mark "PCDL L4672" (number  
average molecular weight: 1990; and OH value: 56.4)  
5 manufactured by Asahi Chemical Industry Co., Ltd.) and  
30.83 g of tolylene diisocyanate, the mixture was  
allowed to react for about 3 hours under heating at 80°C,  
7.42 g of 2-methacryloyl oxyisocyanate was then added,  
and the mixture was further allowed to react for about 3  
10 hours to produce a resin (a2) having a methacryl group  
(having about one intramolecular polymerizable  
unsaturated group per molecule on the average) at the  
end and having a number average molecular weight of  
about 10000. This resin was in the form of thick malt  
15 syrup at 20°C, was fluidized when applying an external  
force, and did not recover its original shape even when  
removing the external force.

[0075]

(Production Example 3)

20 To a 1L separable flask having a thermometer,  
a stirrer and a circulator were added 449.33 g of  
polycarbonate diol (trade mark "PCDL L4672" (number  
average molecular weight: 1990; and OH value: 56.4)  
manufactured by Asahi Chemical Industry Co., Ltd.) and  
25 12.53 g of tolylene diisocyanate, the mixture was  
allowed to react for about 3 hours under heating at 80°C,  
47.77 g of 2-methacryloyl oxyisocyanate was then added,  
and the mixture was further allowed to react for about 3

hours to produce a resin (a3) having a methacryl group (having about two intramolecular polymerizable unsaturated groups per molecule on the average) at the end and having a number average molecular weight of  
5 about 3000. This resin was in the form of thick malt syrup at 20°C, was fluidized when applying an external force, and did not recover its original shape even when removing the external force.

[0076]

10 (Examples 1 to 5)

(Fabrication of Cylindrical Flexographic Printing Original Plate)

To each of the resins (a1) to (a3) obtained in the production examples were added an organic compound  
15 having a polymerizable unsaturated group, porous fine powdered silica (trade mark "Sylosphere C-1504" (hereinafter abbreviated as C-1504; number average particle diameter: 4.5  $\mu\text{m}$ , specific surface area: 520  $\text{m}^2/\text{g}$ ; average pore diameter: 12 nm; pore volume: 1.5  
20 ml/g; ignition loss: 2.5 wt%; and oil absorption: 290 ml/100 g), trade mark "Sylysia 450" (hereinafter abbreviated as CH-450; number average particle diameter: 8.0  $\mu\text{m}$ , specific surface area: 300  $\text{m}^2/\text{g}$ ; average pore diameter: 17 nm; pore volume: 1.25 ml/g; ignition loss:  
25 5.0 wt%; and oil absorption: 200 ml/100 g), and trade mark "Sylysia 470" (hereinafter abbreviated as C-470; number average particle diameter: 14.1  $\mu\text{m}$ , specific surface area: 300  $\text{m}^2/\text{g}$ ; average pore diameter: 17 nm;

pore volume: 1.25 ml/g; ignition loss: 5.0 wt%; and oil absorption: 180 ml/100 g) manufactured by Fuji Silysia Chemical Ltd. as an inorganic porous material, a photopolymerization initiator and other additives as shown in Table 1 to prepare a liquid photosensitive resin composition. A cushion tape having adhesive layers on opposite surfaces was stuck on a cylindrical support having a thickness of 2 mm, an inner diameter of 213.384 mm and a width of 300 mm and made of a glass fiber reinforcement plastic such that air bubbles were kept out. Further, a PET film having a thickness of 100  $\mu\text{m}$  and provided on one surface with an adhesive was wrapped on the cushion tape to be fixed such that the surface with an adhesive was on the front side. The photosensitive resin composition obtained in the manner described above was coated on the PET film in a thickness of 1.9 mm using a doctor blade while rotating the cylindrical support, and a seamless photosensitive resin composition layer was thereby formed to obtain a cylindrical laminate. Further, the surface of the obtained cylindrical laminate was irradiated with an ultraviolet ray from a metal halide lamp (trade mark "M056-L21" manufactured by Eyegraphics Co., Ltd.) in an amount of 4000 mJ/cm<sup>2</sup> (amount integrated using a UV meter and UV-35-APR Filter) in air to fabricate a cylindrical printing original plate. Thereafter, for adjusting the thickness of the printing original plate, cutting was performed using a cemented carbide bite and polishing

was performed using a polishing cloth, whereby a cured photosensitive resin layer having a thickness of 1.7 mm was formed. A carbon dioxide gas laser engraving machine was used to form concavo-convex patterns on the surface of the cylindrical printing original plate thus obtained.

[0077]

The lamp illuminance at the surface of the photosensitive resin composition layer was measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.). The lamp illuminance measured using a filter (trade mark "UV-35-APR Filter") was 100 mW/cm<sup>2</sup>, and the lamp illuminance measured using a filter (trade mark "UV-25 Filter") was 14 mW/cm<sup>2</sup>.

The degree of porosity of the porous fine powdered silica used was 780 for Sylosphere C-1504, 800 for Sylysia 450 and 1410 for Sylysia 470 when calculated with the density set to 2 g/cm<sup>3</sup>.

[0078]

The results of evaluations of printing plates subjected to laser engraving are shown in Table 2. The number of times of wipe of debris after sculpture in Table 2 refers to the number of times of wipe processing required for removing sticky liquid debris generated after sculpture, and if this number of times is large, it means that the amount of liquid debris is large.

In the organic compounds having a double bond used in the examples of the present invention,



derivatives of alicyclic compounds and aromatic compounds are BZMA, CHMA and PEMA.

[0079]

(Example 8)

5           A PET film with an adhesive having a thickness of 125  $\mu\text{m}$  was used as a sheeted support, and the photosensitive resin composition used in Example 1 was coated on the surface of the PET film coated with an adhesive using a doctor blade. Light of 4000  $\text{mJ}/\text{cm}^2$   
10 (value measured using a UV meter and UV-35-APR Filter) as an integrated light amount was applied to the obtained photosensitive resin composition layer in air while moving the metal halide lamp same as that of Example 1 to obtain a cured photosensitive resin layer  
15 having a thickness of 1.7 mm.

[0080]

Patterns were formed on the obtained printing original plate using a carbon dioxide gas laser engraving machine. They were conical favorable patterns  
20 in a pattern portion of fine dots.

A part of the obtained printing plate was cut out to prepare a sample for measurement of the hardness. Using a Zwick automatic hardness meter, a value 15 seconds after the start of the measurement was  
25 determined as the Shore A hardness. As a result, the Shore A hardness was 72 degrees.

The lamp illuminance at the surface of the photosensitive resin composition layer was measured

using a UV meter (trade mark "UV-M02" manufactured by  
ORC Manufacturing Co., Ltd.). The lamp illuminance  
measured using UV-35-APR Filter was 100 mW/cm<sup>2</sup>, and the  
lamp illuminance measured using UV-25 Filter was 14  
5 mW/cm<sup>2</sup>.

[0081]

(Comparative Example 1)

A photosensitive resin composition layer was  
formed in the same manner as in Example 8. A PET cover  
10 film with a release agent having a thickness of 15  $\mu$ m  
was stuck on the obtained photosensitive resin  
composition layer and the same integrated light amount  
of 4000 mJ/cm<sup>2</sup> as in Example 8 was applied to obtain the  
cured photosensitive resin layer.

15 The PET cover film was peeled off, and  
patterns were formed using a carbon dioxide gas laser  
engraving machine. They were conical favorable patterns  
in a pattern portion of fine dots. However, some  
swelling was observed at the portion of fine dots. This  
20 swelling phenomenon is assumed to be caused by the  
liquid debris generated in laser engraving.

[0082]

A part of the obtained printing plate was cut  
out to prepare a sample for measurement of the hardness.  
25 Using a Zwick automatic hardness meter, a value 15  
seconds after the start of the measurement was  
determined as the Shore A hardness. As a result, the  
Shore A hardness was 76 degrees. The value was higher

by 4 degrees than that of Example 8.

The lamp illuminance at the surface of the photosensitive resin composition layer was measured using a UV meter (trade mark "UV-M02" manufactured by  
5 ORC Manufacturing Co., Ltd.). The lamp illuminance measured using UV-35-APR was 100 mW/cm<sup>2</sup>, and the lamp illuminance measured using UV-25 Filter was 0 mW/cm<sup>2</sup>. In the measurement of the lamp illuminance using UV-25 Filter, the illuminance was measured, covering UV-25  
10 Filter with the same PET cover film in consideration of the component absorbed by this cover film because the photosensitive resin composition had been covered with the PET cover film.

[0083]

15 A part of the obtained printing plate on which no patterns were formed was cut out, the cured photosensitive resin was separated from the PET, cooled by liquid nitrogen, and then crushed using a hammer to obtain a powder (G). A powder (H) was obtained in the  
20 same manner from the printing plate of Example 8. The powders (G) and (H) were weighed to the same weight, and were each set in a pyrolysis gas chromatograph apparatus (with a mass spectrometer). This apparatus consists of a pyrolysis apparatus (trade mark "Py-2010D"  
25 manufactured by Frontier Laboratories Ltd), a capillary gas chromatograph apparatus (abbreviated as GC) and a mass spectrometer (abbreviated as MS; trade mark "Automass Sun" manufactured by JEOL LTD.). Each sample

was heated at 250°C for 30 minutes in a heating furnace,  
and a generated gas was collected using a cryo-focusing  
method of trapping the gas with liquid nitrogen. The  
collected gas was analyzed using GC/MS and the amount  
5 thereof was compared. As a result, the collected gas  
was found to be the organic compound (b) in the  
photosensitive resin composition. The analysis by the  
thermogravimetric analysis method (TG method; apparatus  
used for analysis: manufactured by Shimadzu Corporation;  
10 trade mark "TGA-50") showed that the collected gas was  
not heat-decomposed at 250°C, and therefore the gas is  
presumed to be an unreacted organic compound (b). The  
amount of compound presumed to be an unreacted organic  
compound (b) in Example 8 was about one third of that in  
15 Comparative Example 1.

[0084]

(Comparative Example 2)

The photosensitive resin composition was  
photo-cured to form a printing original plate under  
20 conditions different from those of Comparative Example 1  
only in that the lamp was a chemical lamp (trade mark  
"370 Fluorescent Lamp for APR (trade mark "FLR 20S-B-DU-  
37C/M" manufactured by Toshiba Corporation, 20 watt)"  
manufactured by Toshiba Corporation; central wavelength:  
25 370 nm).

The PET cover film was peeled off, and  
patterns were formed using a carbon dioxide gas laser  
engraving machine. They were conical favorable patterns

in a pattern portion of fine dots. However, some swelling was observed at the portion of fine dots. This swelling phenomenon is assumed to be caused by the liquid debris generated in laser engraving.

5 [0085]

A part of the obtained printing plate was cut out to prepare a sample for measurement of the hardness. Using a Zwick automatic hardness meter, a value 15 seconds after the start of the measurement was  
10 determined as the Shore A hardness. As a result, the Shore A hardness was 76 degrees. The value was higher by 4 degrees than that of Example 8.

The lamp illuminance at the surface of the photosensitive resin composition layer was measured  
15 using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.). The lamp illuminance measured using UV-35-APR was 3.1 mW/cm<sup>2</sup>, and the lamp illuminance measured using UV-25 Filter was 0 mW/cm<sup>2</sup>.

[0086]

[Table 1]

	Resin (a)		Organic compound (b)		Inorganic porous material (c)		Polymerization initiator		Other additives	
	Type	Blended amount	Type	Blended amount	Type	Blended amount	Type	Blended amount	Type	Blended amount
Example 1	(a1)	100	PEMA BDEGMA	37 12	C-1504	7.7	DMPAP BP	0.9 1.5	BHT	0.5
Example 2	(a2)	100		Ditto		Ditto		Ditto		Ditto
Example 3	(a3)	100		Ditto		Ditto		Ditto		Ditto
Example 4	(a1)	100	LMA PPMA DEEHEA TEGDMA TMPTMA	6 15 25 2 2	C-1504	7.7		Ditto		Ditto
	(a1)	100	BZMA CHMA BDEGMA	25 19 6	C1504	7.7		Ditto		Ditto
	(a1)	100		Ditto						
	(a1)	100		Ditto						
Example 5	(a1)	100								
Example 6	(a1)	100			CH-450	7.7	DMPAP	1.6	Ditto	
Example 7	(a1)	100			C-470	7.7	DMPAP BP	0.9 1.5	Ditto	

Unit of blended amount in table: parts by weight

(Description of abbreviations)

LMA:	lauryl methacrylate (Mn254)
PPMA:	polypropylene glycol monomethacrylate (Mn400)
DEEHEA:	diethylene glycol-2-ethylhexyl methacrylate (Mn286)
TEGDMA:	tetraethylene glycol dimethacrylate (Mn330)
TMPTMA:	trimethylolpropane trimethacrylate (Mn339)
BZMA:	benzyl methacrylate (Mn176)
CHMA:	cyclohexyl methacrylate (Mn167)
BDEGMA:	butoxydiethylene glycol methacrylate (Mn230)
PEMA:	phenoxyethyl methacrylate (Mn206)
DMPAP:	2,2-dimethoxy-2-phenyl acetophenone
BP:	benzophenone
BHT:	2,6-di-t-butyl acetophenone

[0087]

[Table 2]

	Number of times of wipe of debris after engraving (BEMCOT with ethanol)	Shape of dot portion
Example 1	$\leq 3$	Conical and favorable
Example 2	$\leq 3$	Conical and favorable
Example 3	$\leq 3$	Conical and favorable
Example 4	$\leq 3$	Conical and favorable
Example 5	$\leq 3$	Conical and favorable
Example 6	$\leq 3$	Conical and favorable
Example 7	$\leq 3$	Conical and favorable

[Industrial Applicability]

5 [0088]

The present invention is suitable as a process for producing a cylindrical or sheeted laser engravable flexographic printing original plate, which is suitable for formation of a relief image for a flexographic printing plate by laser engraving, formation of a pattern for surface processing such as embossing, formation of a relief image for printing of a tile or the like, printing of a pattern of a conductor, a semiconductor or an insulator in formation of an electronic circuit, formation of a pattern of a functional material such as antireflection film of an



optical component, a color filter, or a (near) infrared cut filters, and further, coating and formation of a pattern of an oriented film, a ground layer, a luminescent layer, an electron transport layer or a  
5 sealing material layer in production of a display element of a liquid crystal display, an organic electroluminescence display or the like.

[Kind of Document]     Abstract

[Abstract]

[Problem]

Providing a process for producing a printing original plate, which has little amount of remaining organic compounds with unreacted polymerizable unsaturated groups in the cured photosensitive resin layer obtained by applying light, reduced hardness of the cured material and a good laser engravability.

[Solution]

A process for producing a laser engravable flexographic printing original plate, characterized by comprising the steps of: forming a photosensitive resin composition layer on a cylindrical support or a sheeted support; applying light to the formed photosensitive resin layer to form a cured laser engravable photosensitive resin layer; and then adjusting a thickness of the cured photosensitive resin layer and shaping a surface of the cured photosensitive resin layer, wherein the light applied to the photosensitive resin layer includes light having a wavelength of 200 nm or more and 450 nm or less, and an illuminance of light at a surface of the photosensitive resin layer is 20 mW/cm<sup>2</sup> or more when measured using a UV meter (trade mark "UV-M02" manufactured by ORC Manufacturing Co., Ltd.) and UV-35-APR Filter, and 3 mW/cm<sup>2</sup> or more when measured using the UV meter and UV-25 Filter.

[Selected Drawing]    There is no selected drawing.